

Anisole hydrodeoxygenation over supported CoMo catalysts: effect of Co/Mo ratio and support on catalyst stability and activity

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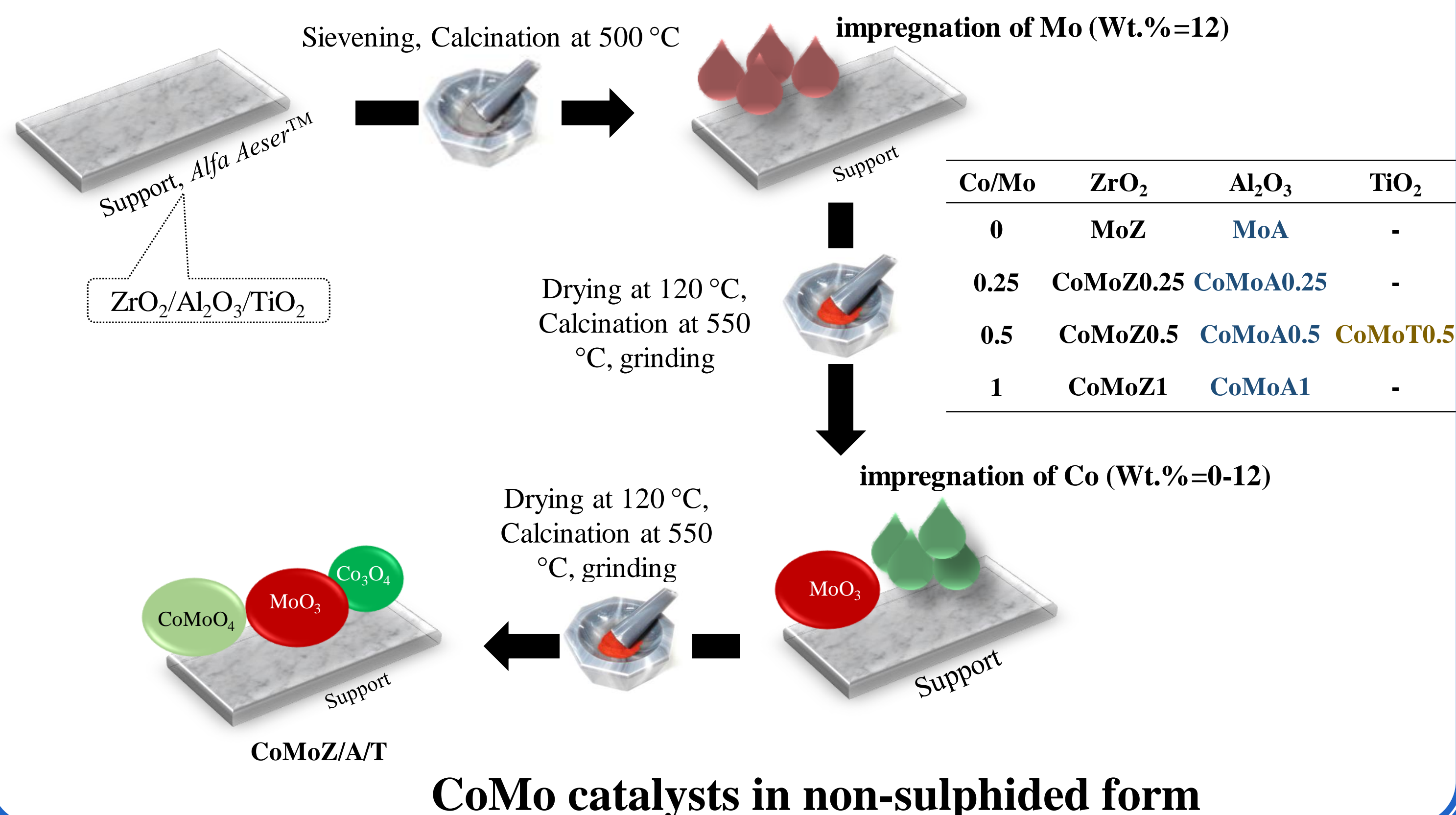
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Introduction



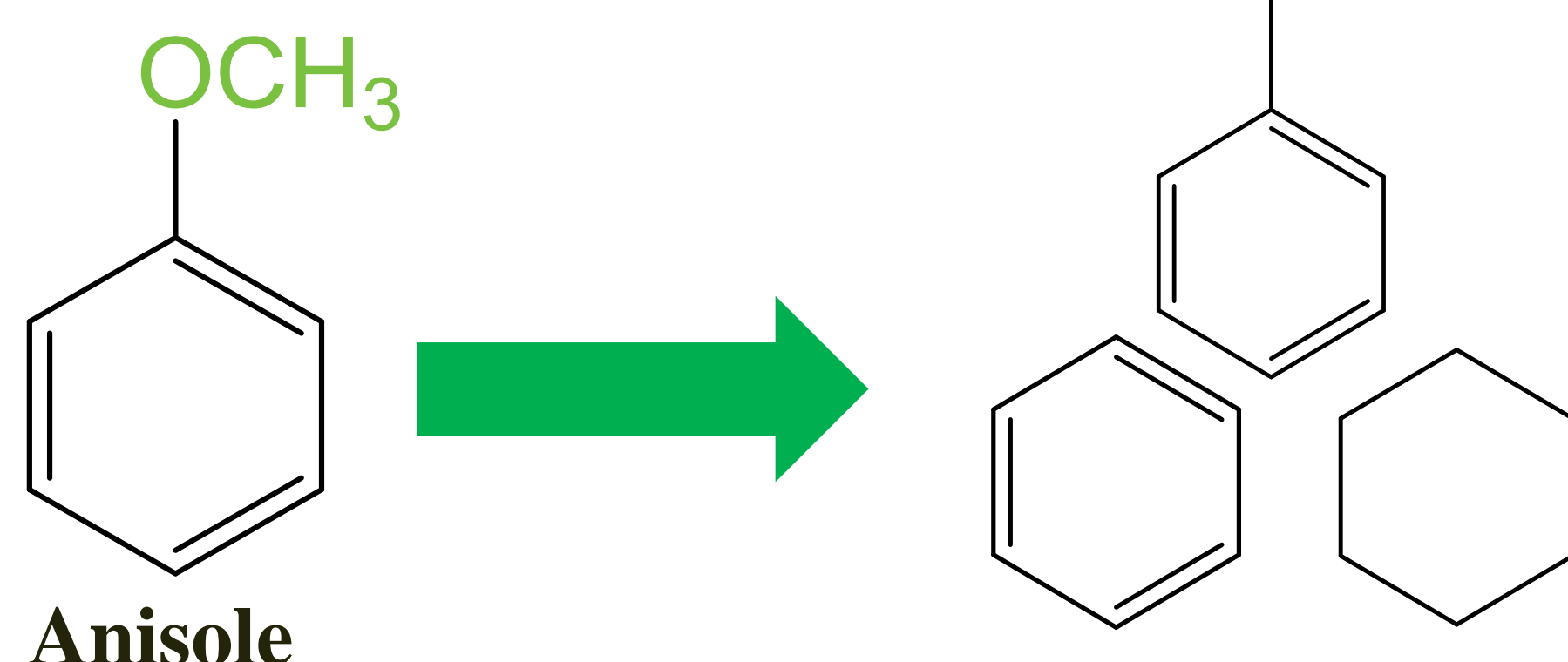
Catalyst Preparation

Sequential Inception Wet Impregnation of Mo and Co



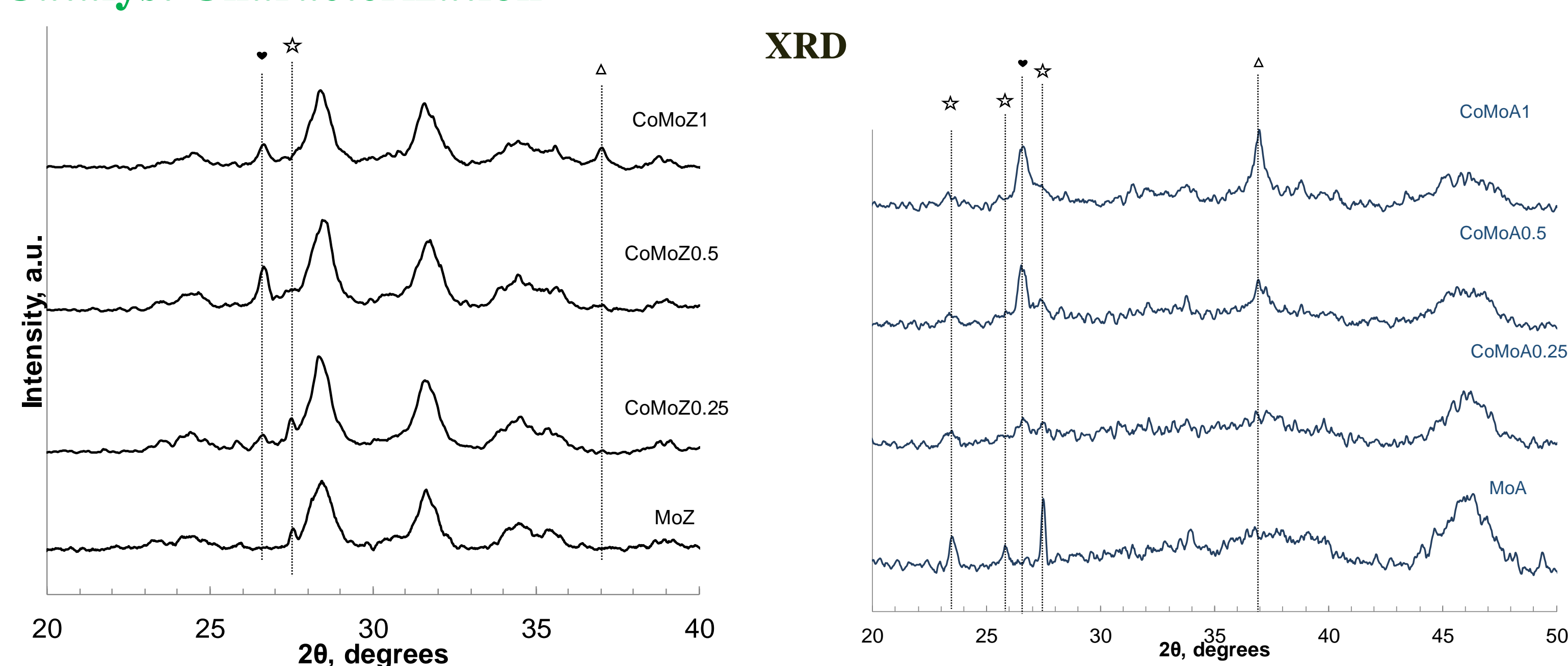
Rationale:

- ✓ Anisole is one of the most common chemical structure found in lignocellulosic biomass and challenging to perform deep HDO
- ✓ Co addition in systematic way to identify and enhance the stable & active phases of MoO₃ catalysts for oxygenate HDO



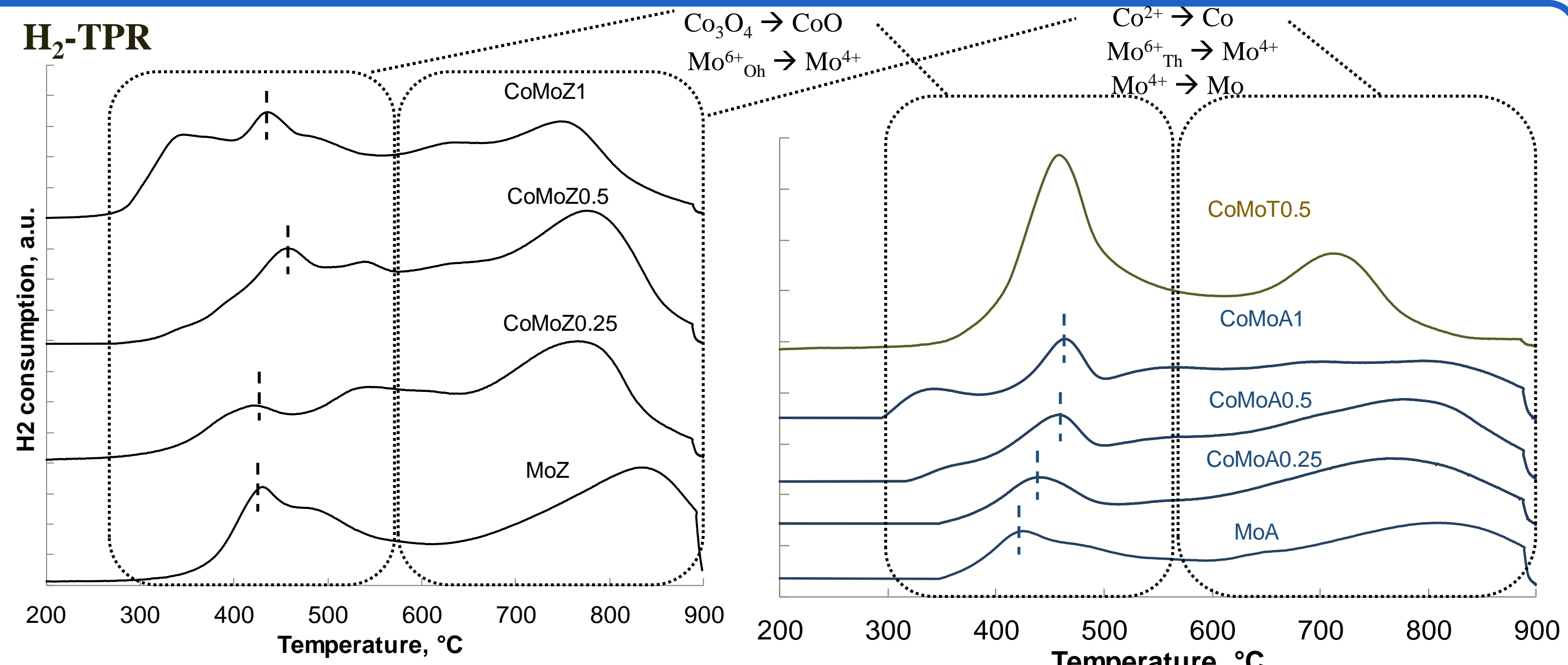
Catalyst Characterization

Aim: Stable catalyst with high HDO selectivity



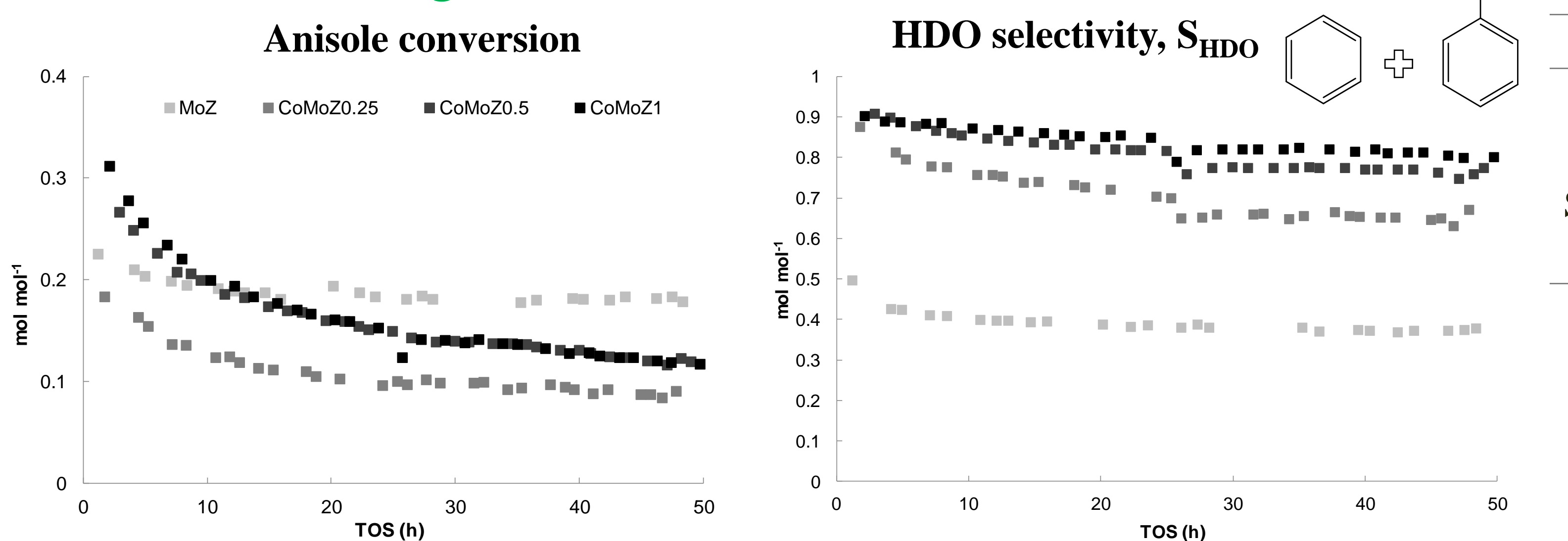
- ✓ MoO₃ crystallites disappear as Co loading increases
- ✓ Mixed oxide (CoMoO₄) crystallizes at higher Co loadings.

H₂-TPR



- ✓ Mo⁶⁺ reduction temperature increases with Co loading
- ✓ Mo⁶⁺ exists in MoO₃, CoMoO₄, and also in mixed form with support

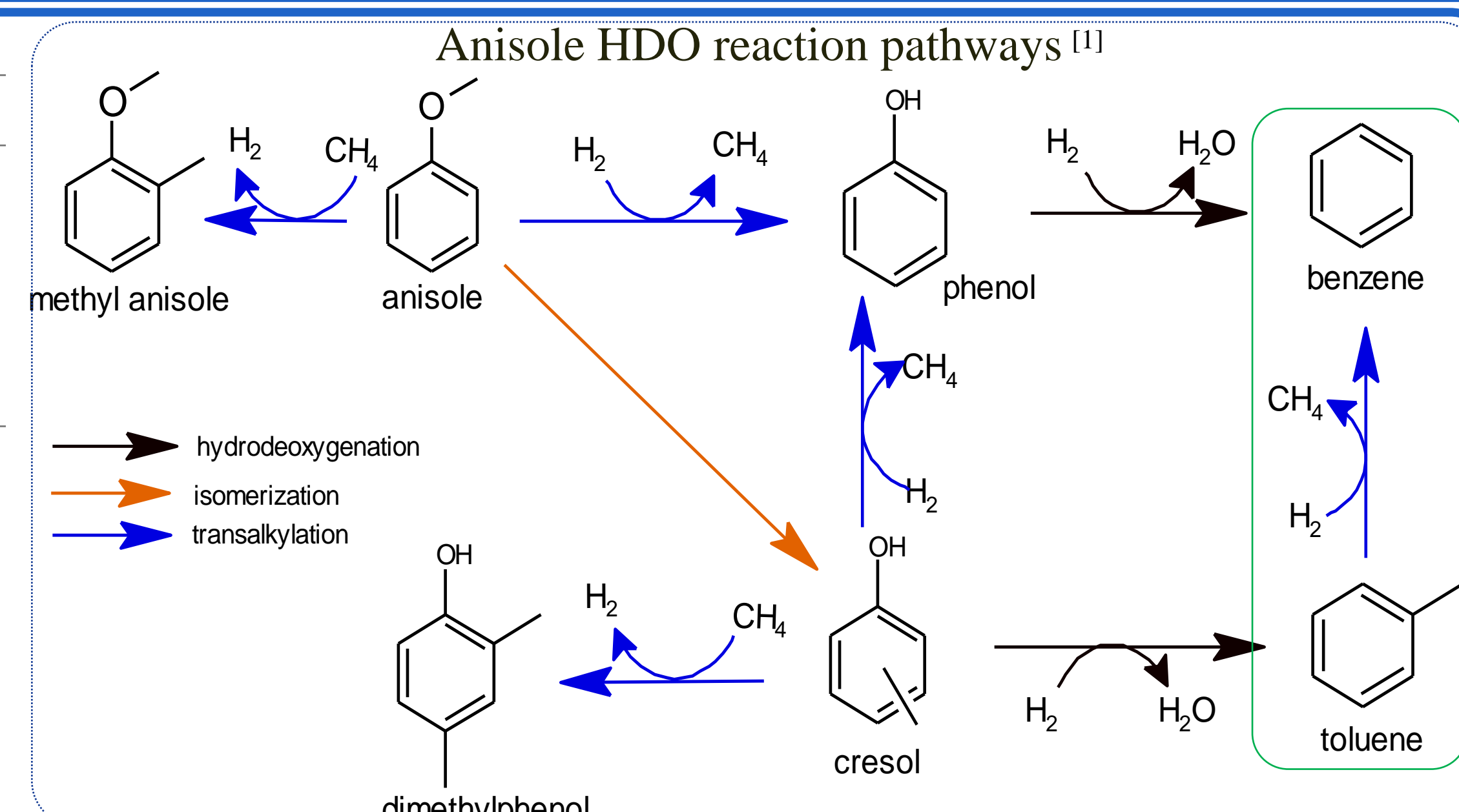
Performance testing and Discussion



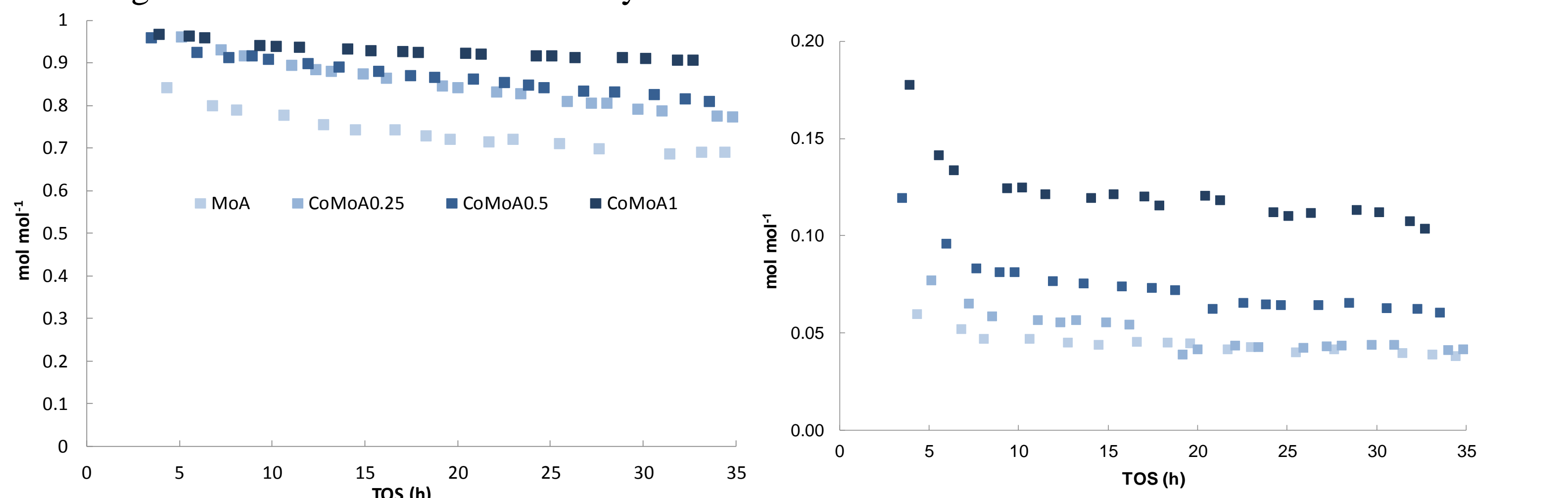
Operating conditions

Temperature (°C)	340
Pressure (MPa)	0.5
Space time (kg _{cat} /s/mol _{anisole})	20-230
H ₂ /anisole (mol _{mol} ⁻¹)	50

$$S_{HDO} = \frac{\sum F_{O \text{ free product}}}{F_{in \text{ anisole}} - F_{out \text{ anisole}}}$$

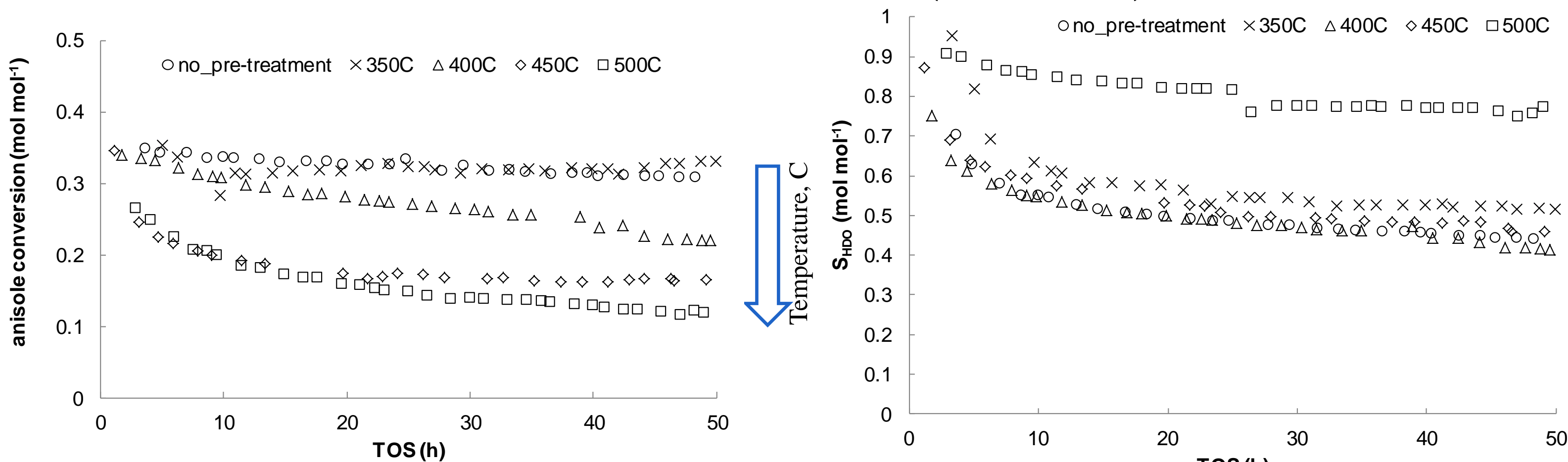


- ✓ Decrease in catalyst stability while an increase in HDO product selectivity with addition of Co
- ✓ No significant increase in HDO activity observed at Co/Mo > 0.5



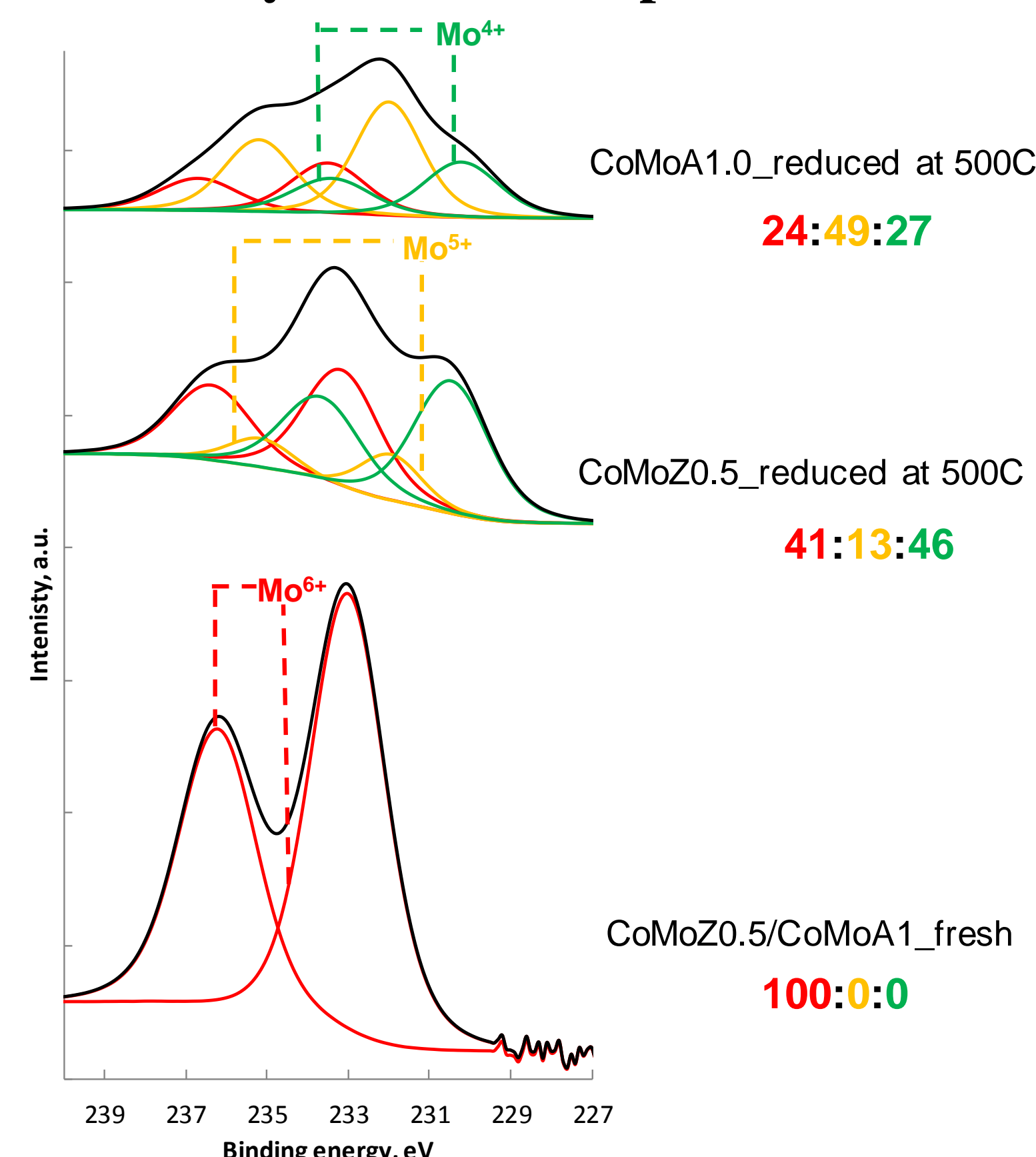
- ✓ Higher conversions and increase in HDO product selectivity with addition of Co
- ✓ Initial rapid decrease in HDO product selectivity with TOS

Pre-treatment effect (CoMoZ0.5)



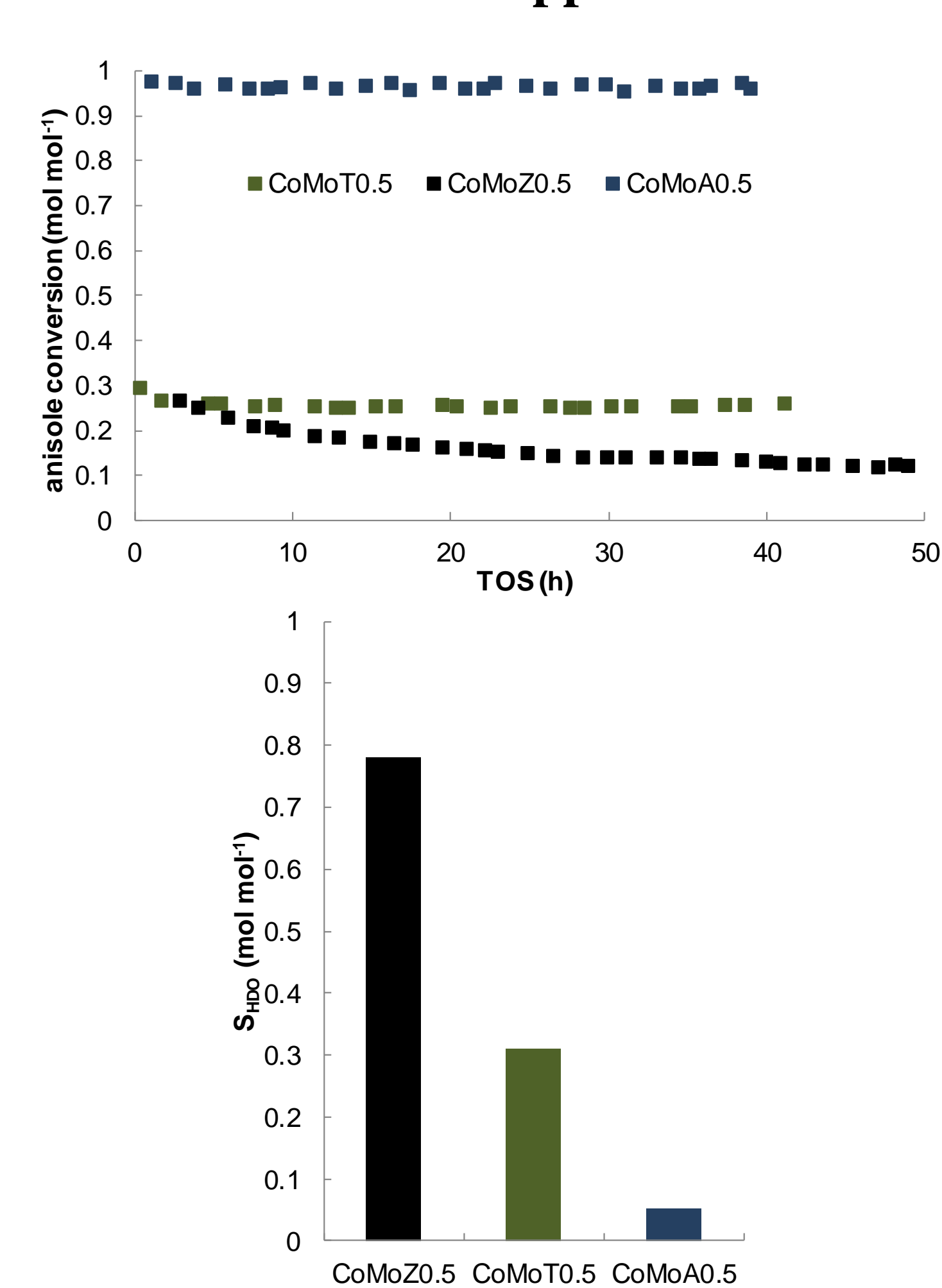
- ✓ Increase in catalyst stability while a decrease in HDO product selectivity with reduction at < 350 °C
- ✓ Reduction at higher temperatures (500 °C) → higher HDO activity, low overall conversion

Catalyst surface composition



- ✓ Catalyst stability, Overall conversion enhanced with high Mo⁵⁺ quantity
- ✓ HDO selectivity enhanced with high Mo⁴⁺ quantity

Effect of support



- ✓ Initial anisole conversion: Al₂O₃ > TiO₂ ≈ ZrO₂
- ✓ Total HDO selectivity: ZrO₂ > TiO₂ > Al₂O₃

Conclusions

- ✓ Co addition: i) Increase in the HDO activity for Mo oxide catalysts, ii) Decrease in catalyst stability and overall conversions compared to MoZ for CoMoZ catalysts, iii) Increase in catalyst stability and overall conversions compared to MoA for CoMoA catalysts
- ✓ Higher reduction temperatures favor higher HDO activity for CoMoZ catalysts
- ✓ ↑Mo⁵⁺ → stable catalyst and high anisole conversions, ↑Mo⁴⁺ → high HDO activity

Acknowledgements

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